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OSMOTIC PRESSURE MEASUREMENTS of GLUCOSE SOLUTIONS at 10° and 20°.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH A REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

By

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OSMOTIC PRESSURE MEASUREMENTS of GLUCOSE SOLUTIONS at 10° and 20°.

The Cells.[1]

The cells used in the following experiments are made of a mixture of equal parts of a fire clay from Dorsey, Maryland, and a ball clay from Edgar, Florida. The clays are elutriated separately in an inclined wooden trough divided into compartments and the finer constituents of the clays thus obtained are bolted through Nos. 10, 14, and 16 silk bolting cloth, the latter having 24,336 holes to the square inch. The bolted clay is allowed to subside and the water above it drawn off by means of a siphon. Most of the water remaining in the clay is removed by the method of "electrical endosmose," which is as follows: A large porous pot is placed in a larger porcelain dish. The clay in the form of a thick porridge is poured into the pot and two electrodes are inserted, the anode into the clay and the cathode into the water which collects in the outer vessel. More clay is introduced from time to time and the water in the outer dish is kept at a constant level by means of an automatic siphon. When so much water is removed that cracks begin to appear in the clay, it is packed down with a pestle. A fall in potential of 110 volts is employed.

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[1] For a detailed description see H. N. Morse: Carnegie Publication, No. 198.

After drying by heat the two clays are now mixed in equal proportions by weight in the following manner: Equal weights are sifted; the mixture is churned with water for several hours and bolted through Nos. 14 and 16 bolting cloth; the material is dried by "endosmose," as described above, and is kneaded to a putty on a plate glass surface. The clay is now tamped down in the steel cylindrical press and as much water as possible is forced out by means of a wrench. The press is then placed in the compressing apparatus and the clay subjected to a pressure of 20 tons upon each square inch of its surface. The first descent of the weight is accomplished in about 2 hours and the second in about 16 hours. The same results may be secured by lighter weights and longer pressing, or heavier weights and shorter pressing. The clay cylinder is removed from the press and is cut to form on the lathe.

The cutting of the cells from the cylinders requires extreme care. The cell wall must not be weakened at any point by the pressure of the cutting tools because, when the cell is baked, shrinkage takes place and the shrinking material draws away from regions of weakness and cracks are developed. To avoid this the cutting tools must have the proper "clearance" and the cell must never "sag."

The cells are baked at the kilns of the Bennett Pottery Company at a temperature of about 1300 degrees, or between the melting points of Seger cones Nos. 8 and 9. After baking the cells are mounted on the lathe and ground with a carborundum wheel to fit the brass rings with which the manometers are attached and to

fit the cones upon the ends of the manometers. The glaze used must have the same coefficient of expansion as the cell, otherwise "crazing" results. A mixture of silica and feldspar added to one of the glazes used by the potters upon white tableware satisfies the requirement, and at the present time the glazing as well as the baking is done at the potteries.

Cells, when manufactured as described, have three necessary characteristics: (1) Great and uniform strength of wall; (2) The absence of "air blisters;" (3) A very fine and perfectly uniform wall texture to insure the meeting of the anion and cation just within the inner mouths of the pores. The necessity of great strength of wall is obvious, as is the elimination of air blisters which cause the deposition of subsidiary membranes in the interior of the cell wall. The necessity of forming the membrane at the interior surface of the cell wall is evident because, if it be located within the wall, the solution near the membrane, owing to the slowness of diffusion, will be less concentrated than the solution within the cell proper and, as a result, it would not be possible to know the final concentration of any solution placed in the cell. If the pores were of such size that the anion and cation would meet on the inner surface of the cell wall, the membrane would lack strength and be easily ruptured. This latter condition is realized if the pores are too small , so that to fulfill condition (3) the wall texture must not be too fine or too coarse and must be perfectly uniform.

The Membranes.[2]

The first step toward the deposition of the membrane is the removal of air from the pores of the cell and its replacement by water. This is accomplished by electrolyzing dilute solutions of salts, the result of which is the transportation of a volume of water by the cation of the salt used. The salt chosen is lithium sulphate because it has been shown that "the volumes of water carried through the porous wall of a cell, under identical conditions, are inversely proportional to the relative velocities of the various cations divided by their respective valencies." A 0.005 normal solution is employed. The cell is filled with the solution and immersed in it as far as the glazed portion. The electrodes are of platinum, the one within the cell serving as the cathode. The water drawn into the cell is automatically removed by means of a siphon. The liquid thus obtained is mixed from time to time with the solution outside of the cell. When the water has been removed from the pores the cell is emptied, rinsed, soaked for a time in distilled water and then filled with and immersed in pure water, and the electrolysis resumed. When the conductivity has fallen to that of distilled water, the cell is ready for the deposition of the membrane.

The apparatus for the deposition of the membrane is as follows: The anode, in the form of a copper cylinder, is placed in an empty glass vessel, and within the cylinder is placed the cell which is closed by a rubber stopper containing a funnel with a stem reaching nearly to the bottom of the cell, a platinum cathode and an overflow

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[2] Ibid.

tube. The cell and the glass vessel are filled with one-tenth normal solutions of potassium ferrocyanide and copper sulphate, and the circuit is closed. A voltage of 110 is used.

The resistance at first is high owing to the fact that in the beginning the cell wall is filled with nearly pure water, but it soon falls and then rises again as the formation of the membrane progresses. Within an hour or two the resistance reaches a maximum and then begins to fall probably owing to an accumulation of alkali within the membrane itself. To prevent this as far as possible during the electrolysis, the ferrocyanide is renewed every five minutes through the funnel. When the maximum resistance is reached the circuit is broken and the cell is allowed to soak for several days in thymol water, the water being frequently renewed. The thymol water is an effectual preventative against infection by "pencillium" which otherwise is liable to attack the membranes and soon destroys them. After three days the membrane forming process is repeated and the maximum resistance on this occasion is generally higher than that attained in the first electrolysis. The cell is placed in water again for three days and the alternate "running" and "soaking" continued until a final maximum resistance is reached which can be forced no higher. The maximum resistance finally attained varies greatly with the temperature, but is generally over 100,000 ohms.

The cell is now ready to be set up for "seasoning" the membrane under pressure. The cell is set up with a concentrated

solution of glucose to which a small amount of ferrocyanide is added which is isosmotic with respect to the copper sulphate dissolved in the thymol water in which the cell is to stand. After the contents of the cell are subjected to a considerable mechanical pressure, it is then placed in a constant temperature bath and allowed to cane to equilibrium. Eventually the meniscus comes to rest at a point generally below the position it should have, showing that the membrane has probably broken under pressure and has been mended by the "membranogens." This would cause a dilution of the contents of the cell and explain the fact that the solution does not develop the full osmotic pressure of the original solution. Whatever the result of the trial the cell is emptied, rinsed and soaked for several days in thymol water. The membrane forming process is then repeated and the cell set up again under pressure. In this way the cell is developed in about a month's time so that it will register full osmotic pressure and in which solutions undergo no dilution.

The membrane is developed at the temperature at which it is to be used for the measurement of pressure, and this necessitates keeping all of the solutions that are to be used with it at temperature also. The much repeated "soaking" is of great benefit to the membrane that cannot be dispensed with. A possible explanation of this is that the water extracts any alkali in the membrane and enables it to retain its colloidal condition which is necessary for semi-permeability.

The membranes vary greatly as regards their speed in attaining equilibrium. Other things being equal, water passes more

slowly through a membrane in a hard burned cell in which the pores are small than it does through a soft burned cell in which the pores are large. Again, the rate of passage of water through a membrane decreases with the latter's age and use. Electrolytes also render a membrane sluggish.

The Manometers.[3]

The manometers used for the measurement of osmotic pressure have a bore of about .6 millimetre and a calibrated portion that ranges from 400 to 500 millimetres. Tubes of small bore are used because: (1) Short columns of mercury are introduced into the upper ends of the manometers in order to protect the calibrated portion of the tubes when they are closed. If the bore is large, the mercury is often dislodged by the severe tapping to which the manometers are subjected; (2) When the small volume of gas contained in the manometers is compressed, there results but little dilution of the solution in the cell; (3) Small amounts of mercury are required by manometers of small bore. The disadvantages of using tubes of small bore are : (1) It is more difficult to deal with the meniscus in a narrow tube; (2) The capillary depression is large in small tubes; (3) The movements of the mercury are greatly affected by the presence of impurities.

The mercury used in the manometers is purified as follows: (1) It is filtered through paper, air is forced through it at boiling temperature and the mercury is filtered again; (2) It is distilled in a vacuum; (3) The distillate is passed in a fine

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[3] Ibid.

stream 1,000 times through a solution containing 2 percent. nitric acid and 2 per cent. mercurous nitrate; (4) The mercury is distilled again in a vacuum using a new still. The mercury thus purified retains its luster in the air and is highly satisfactory. The bore of the tubes should be uniform and circular throughout, but neither of these conditions is very seldom realized.

The first step in calibrating a manometer is to etch upon it two fine lines extending around the tube. These lines are called the "scratches" and all readings are referred to one or the other of them. No other graduation appears upon the manometer. The bore of the tube is now calibrated by setting a thread of mercury exactly end to end and determining its length until the thread has passed along the tube the entire distance between the two scratches. It is then run out of the tube and weighed. Afterwards the whole of the calibrated portion of the manometer is filled with mercury, which is also run out and weighed. The mean diameter of the bore is calculated from the length and weight of the long thread, and from the observed length of the small thread in different parts of the tube a mean calibration unit is derived and a curve of corrections made. Finally, a mean correction for the double meniscus is obtained from the weight and length of the long and short threads. "If we multiply the weight of the short thread by the number of times its length is contained in the long thread, i.e., by the number of times it was set end to end, and subtract the product from the weight of the long thread, the difference is the weight of the mercury which would be required to fill all the meniscus spaces which were left vacant in setting the short thread end to end along the tube. Converting this difference in weight

into volume, and dividing by the number of settings less one, we obtain a mean connection for a double meniscus, which is the meniscus connection to be applied in all measurements of pressure since the nitrogen in the manometers is always included between two mercury columns."

The capillary depression of the manometer is then determined. It is filled with pure mercury and is connected to a glass tube, having an internal diameter of 35 millimetres, by means of a rubber tube filled with mercury and reinforced with tape. This side tube enables the manipulator to adjust the mercury in the tube under examination to any desired height. The arrangement is placed in a constant temperature bath and the difference in height between the mercury in the manometer and that in the side tube is noted at points a few millimetres apart along the whole of the calibrated portion of the manometer. From the observed data a capillary depression curve is constructed and used (1) in determining the volume of the manometer, and (2) in correcting its volume under an unknown pressure.

Pure nitrogen is now introduced into the manometer, a little mercury is run in after it and the tube is sealed. The volume of the manometer is determined by placing it in a bath of constant temperature and subjecting it to many known pressures of low magnitude.

Connection between manometer and cell is made by means of a brass cone which is covered with rubber and through which pass the manometers and also a very small brass tube terminating in a large threaded head. The two are held in place by Wood's metal.

The small tube allows some of the solution to escape from the cell, when desirable, after connection between the manometer and cell has been made. The cone is forced tightly down into the cell by means of a brass collar and nut, forming a tight joint after the brass tube is closed by means of a screw plug with washer.

Regulation of Temperature.[4]

The principle of temperature regulation is as follows: "If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heating surface which is more efficient than the cooled one, but which is under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid in the work either of the cooling or of the heating surface."

Since a closed osmotic cell is in some respects analagous to a sensitive thermometer, accurate regulation of the bath is necessary in order to prevent "thermometer effects" which take place with fluctuation in temperature and which develop in the cell a

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[4] Ibid.

condition of over or under pressure. These phenomena may be understood by stating (1) that the capacity of a closed cell is a fixed quantity; (2) that every change in volume of the cell contents, due to rise or fall in temperature, is followed by a passage of solvent through the membrane which changes the osmotic pressure of the solution; and (3) that the passage of the solvent through the membrane is a much slower process than the changes in volume of the solution in the cell with change in temperature.

The type of bath used in the present work is about six feet long, five feet high, and 22 inches wide, made of heavy white pine and built in two sections, the upper being the "air space," and the lower the water compartment, which projects 15 inches beyond the upper to allow the placing of the pumping mechanism. Both compartments are lined throughout with tinned copper and are separated by a stout brass plate. This plate rests on top of the water compartment on rubber packing and carries the two parallel copper troughs which extend down into the water compartment and into which the cells with their manometers are placed. The thermostat and thermometer also project into the water through holes in the brass plate, and are fixed tightly in place by means of corks.

From the above description it is seen that the water compartment is effectually closed, and that the air space above will never become saturated with or even contain an appreciable amount of water vapor, no matter at what temperature the bath may be running. If such were not the case, when the insulating pads are removed from the glass door in order to read the manometers,

moisture might condense on the inside of the glass and, as a result, would interfere with accurate readings by means of the cathetometer. The interior of the bath is reached through a door made of heavy plate glass and running downward. The top is high enough to avoid the necessity of raising it when the cells are placed in the bath.

The cooling system of the water compartment consists of a parallel series of pipes lying on the bottom of the compartment and through which hydrant water runs at constant pressure. The heating system consists of two copper cylinders within which are placed electric lamps and which extend down into the water. The water is constantly circulated by means of a pump first over the cooling surface, and then over the heating surface. The temperature of the air space is regulated independently of that of the water. The cooling surface is identical to that used in the water compartment except that the pipe system is placed at the top of the air space. The constant source of heat within the air space is a pair of shaded electric lamps placed directly before an electric fan which keeps the air in circulation.

The thermostats are of large volume and the liquid used is tolnene with mercury for electrical contact, rendering them very sensitive. The contact of the platinum wire in both thermostats is spanned by an electric light which effectually prevents sparking. The capillary was, nevertheless, cleaned regularly, and both thermostats worked perfectly throughout the whole investigation. The thermometers were calibrated against standards from the U. S. Bureau of Standards. The constancy of temperature was in general very satisfactory. The maximum deviation observed for periods of

six or seven days was often less than ± 0.02 of a degree. The variations at other times was much greater, but in such cases was generally traceable to some other cause, though not always. At first some difficulty was experienced in obtaining a constant flow of hydrant water through the cooling systems, but the trouble was successfully overcome.

The Weight Normal System for Solutions.[5]

A short account of how Morse and Frazer were led to the adoption of the weight normal system is as follows: "Soon after beginning the measurements of the osmotic pressure of cane sugar under conditions which gave to the results a considerable degree of precision, it became apparent that the mass of the solvent plays a part which appears to have been unsuspected hitherto. We found - or appeared to discover - that a gram-molecular weight of the substance, dissolved in water and diluted to a litre volume, is not the normal standard for osmotic pressure. On the other hand, when we dissolved a gram-molecular weight of cane sugar (342.22 grams) in 1,000 grams of water, i.e., in that mass of the solvent which has the unit volume one litre at the temperature of maximum density, we found its osmotic pressure at about 20 degrees in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to one litre; i.e., to that volume which the unit mass of the solvent has at the temperature of greatest density."

Thus the change from volume normal to weight normal was made

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[5] Ibid.

and now we always have the same mass of solvent coming into play, no matter what the concentration of the solution. We have, in other words, corrected experimentally for the b in the van der Waal's equation as applied to solutions $(p + \frac{a}{v^2})(v - b) =$ constant, in which b is the volume of the dissolved molecules. For this reason the glucose solutions used in this investigation have been prepared according to the weight normal system.

The Measurements.

Table I.

0.1 Wt. normal solution. Expt. 1 at 20°. Cell I_6. Resistance, 110,000 ohms. Manometer 60. Calc. gas pressure, 2.39 atms. Time of setting up cell, Dec. 2, 1914. Initial pressure, 3.527 atms. Observed osmotic pressures:

Atms.	Atms.	Atms.
Dec. 27, 2.339	Dec. 31, 2.405	Jan. 5, 2.420
28, 2.401	Jan. 2, 2.429	8, 2.412
29, 2.416	3, 2.427	9, 2.410
30, 2.416	4, 2.431	(11 days)

Mean osmot. pressure, 2.415 atms.

Corr. mean osmot. pressure, 2.485 atms.

Mean ratio of osmotic to gas pressure, 1.039.

Table II.

0.1 Wt. normal solution. Expt. 2 at 20°. Cell 4. Resistance, 183,000 ohms. Manometer 61. Calc. gas pressure, 2.39 atms. Time of setting up cell, Jan. 10, 1915. Initial pressure, 2.539 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Jan. 25, 2.41	Jan. 28, 2.421	Jan. 31, 2.421
26, 2.405	29, 2.418	Feb. 1, 2.419
27, 2.416	30, 2.41	(8 days)

Mean osmot. pressure, 2.415 atms.

Corr. mean osmot. pressure, 2.477 atms.

Mean ratio of osmotic to gas pressure, 1.032.

Mean ratio of Expts. 1 and 2, 1.035.

Table III.

0.1 Wt. normal solution. Expt. 1 at 10°. Cell 14. Resistance, 182,000 ohms. Manometer 60. Calc. gas pressure, 2.308 atms. Time of setting up cell, Jan. 18, 1915. Initial pressure, 2.34 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Jan. 24, 2.34	Jan. 28, 2.326	Feb. 1, 2.327
25, 2.345	29, 2.318	2, 2.322
26, 2.325	30, 2.315	3, 2.322
27, 2.315	31, 2.312	4, 2.310
		(12 days)

Mean osmot. pressure, 2.3231 atms.

Corr. mean osmot. pressure, 2.388 atms.

Mean ratio of osmotic to gas pressure, 1.034.

Table IV.

0.2 Wt. normal solution. Expt. 1 at 20°. cell A_6. Resistance, 275,000 ohms. Manometer 40. Calc. gas pressure, 4.78 atms. Time of setting up cell, Nov. 10, 1914. Initial osmot. pressure, 5.731 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Nov. 22, 4.91	Nov. 25, 4.904	Nov. 28, 4.891
23, 4.932	26, 4.933	Dec. 3, 4.922
24, 4.925	27, 4.94	(8 days)

Mean osmot. pressure, 4.9188 atms.

Mean ratio of osmotic to gas pressure, 1.0296.

Table V.

0.2 Wt. normal solution. Expt. 2 at 20°. Cell X_6. Resistance, 157,000 ohms. Manometer 43. Calc. gas pressure, 4.78 atms. Time of setting up cell, Nov. 10, 1914. Initial pressure, 4.835 atms. Observed osmot. pressures:

	Atms.		Atms.		Atms.
Nov. 22,	4.97	Nov. 25,	4.915	Nov. 28,	4.889
23,	4.90	26,	4.877	Dec. 3,	4.911
24,	4.895	27,	4.885	4,	4.899
					(9 days)

Mean osmot. pressure, 4.8934 atms.

Corr. mean osmot. pressure, 4.940 atms.

Mean ratio of osmotic to gas pressure, 1.033.

Table VI.

0.2 Wt. normal solution. Expt. 3 at 20°. Cell 2. Resistance, 157,000 ohms. Manometer 40. Calc. gas pressure, 4.78 atms. Time of setting up cell, Dec. 22, 1914. Initial pressure, 4.095 atms. Observed osmot. pressures:

	Atms.		Atms.		Atms.
Jan. 16,	4.792	Jan. 19,	4.81	Jan. 22,	4.783
17,	4.80	20,	4.80	23,	4.794
18,	4.819	21,	4.79		(8 days)

Mean osmot. pressure, 4.7985 atms.

Corr. mean osmot. pressure, 4.915 atms.

Mean ratio of osmotic to gas pressure, 1.028

Mean ratio of Expts. 1, 2, and 3, 1.030.

Table VII.

0.3 Wt. normal solution. Expt. 1 at 20°. Cell X_6. Resistance, 157,000 ohms. Manometer 44. Calc. gas pressure, 7.170 atms. Time of setting up cell, Jan. 13, 1915. Initial pressure, 7.68 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Jan. 20, 7.336	Jan. 27, 7.304	Jan. 30, 7.324
21, 7.351	28, 7.307	31, 7.332
22, 7.353	29, 7.323	Feb. 1, 7.349
		(10 days)

Mean osmot. pressure, 7.3358 atms.

Corr. mean osmot. pressure, 7.393 atms.

Mean ratio of osmotic to gas pressure, 1.031.

Table VIII.

0.3 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 122,000 ohms. Manometer 44. Calc. gas pressure, 7.170 atms. Time of setting up cell, Feb. 8, 1915. Initial pressure, 8.327 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Feb. 15, 7.457	Feb. 19, 7.313	Feb. 23, 7.374
16, 7.344	20, 7.365	24, 7.377
17, 7.355	21, 7.377	(10 days)
18, 7.277	22, 7.362	

Mean osmot. pressure, 7.360

Mean ratio of osmotic to gas pressure, 1.026

Mean ratio of Expts. 1 and 2, 1.028.

Table IX.

0.4 Wt. normal solution. Expt. 1 at 20°. Cell D_6. Resistance, 122,000 ohms. Manometer 37. Calc. gas pressure, 9.56 atms. Time of setting up cell, Feb. 17, 1915. Initial pressure, 10.143 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Feb. 22, 9.717	Feb. 26, 9.620	March 2, 9.655
23, 9.701	27, 9.651	5, 9.596
24, 9.706	March 1, 9.635	6, 9.616

Mean osmot. pressure, 9.6159 atms.

Mean ratio of osmotic to gas pressure, 1.010.

Table X.

0.4 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 91,000 ohms. Manometer 37. Calc. gas pressure, 9.56 atms. Time of setting up cell, March 10, 1915. Initial pressure, 10.342 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
March 16, 9.637	Mar. 25, 9.622	Mar. 31, 9.600
17, 9.765	26, 9.581	April 1, 9.617
18, 9.684	29, 9.693	2, 9.603
24, 9.676	30, 9.580	3, 9.602

Mean osmot. pressure, 9.638 atms.

Corr. mean osmot. pressure, 9.734 atms.

Mean ratio of osmot. to gas pressure, 1.018.

Mean ratio of Expts. 1 and 2, 1.014.

Table XI.

0.5 Wt. normal solution. Expt. 1 at 20°.. Cell 1. Resistance, 183,000 ohms. Manometer 30. Calc. gas pressure, 11.95 atms. Time of setting up cell, Jan. 15, 1915. Initial pressure, 13.103 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Jan. 20, 12.26	Jan. 27, 12.156	Jan. 31, 12.254
21, 12.27	28, 12.193	Feb. 1, 12.278
22, 12.216	29, 12.22	(10 days)
23, 12.181	30, 12.212	

Mean osmot. pressure, 12.224 atms.

Mean ratio of osmotic to gas pressure, 1.023

Table XII.

0.5 Wt. normal solution. Expt. 2 at 20°. Cell X_6. Resistance, 137,500 ohms. Manometer 30.. Calc. gas pressure, 11.95 atms. Time of setting up cell, Feb. 17, 1915. Initial pressure, 12.582 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Feb. 25, 12.259	March 2, 12.226	March 6, 12.183
26, 12.237	3, 12.151	8, 12.196
27, 12.146	4, 12.191	(10 days)
March 1, 12.172	5, 12.194	

Mean osmot. pressure, 12.195 atms.

Mean ratio of osmotic to gas pressure, 1.021.

Table XIII.

0.5 Wt. normal solution. Expt. 3 at 20°. Cell 2. Resistance, 200,000 ohms. Manometer 44. Calc. gas pressure, 11.95 atms. Time of setting up cell, March 2, 1915. Initial pressure, 15.376 atms.

Observed osmot. pressures:

Atms.	Atms.	Atms.
March 9, 12.371	March 12, 12.391	March 19, 12.229
10, 12.362	13, 12.370	20, 12.211
11, 12.474	15, 12.455	21, 12.206

Mean osmot. pressure, 12.3069 atms.

Mean ratio of osmotic to gas pressure, 1.0298.

Mean ratio of Expts. 1, 2, and 3, 1.0246.

Table XIV.

0.6 Wt. normal solution. Expt. 1 at 20°. Cell 4. Resistance, 137.500 ohms. Manometer 30. Calc. gas pressure, 14.337 atms. Time of setting up cell, Dec. 11, 1914. Initial pressure, 14.122 atms.

Observed osmot. pressures:

Atms.	Atms.	Atms.
Dec. 23, 14.751	Dec. 27, 14.774	Dec. 31, 14.732
24, 14,783	28, 14.710	Jan. 3, 14.730
25, 14.810	29, 14.735	4, 14.753
26, 14.771	30, 14.747	(11 days)

Mean osmot. pressure, 14.754 atms.

Corr. mean osmot. pressure, 14.851 atms.

Mean ratio of osmotic to gas pressure, 1.035.

Table XV.

0.6 Wt. normal solution. Expt. 2 at 20°. Cell J_6. Resistance, 183,000 ohms. Manometer 45. Calc. gas pressure, 14.339 atms. Time of setting up cell, March 2, 1915. Initial pressure, 15.763 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
March 8, 14.793	March 12, 14,679	March 16, 14.845
9, 14.649	13, 14.670	18, 14.778
10, 14.622	14, 14.786	(10 days)
11, 14.734	15, 14.876	

Mean osmot. pressure, 14.743 atms.

Mean ratio of osmotit to gas pressure, 1.0281.

Mean ratio of Expts. 1 and 2, 1.031.

Table XVI.

0.7 Wt. normal solution. Expt. 1 at 20°. Cell E_6. Resistance, 220,000 ohms. Manometer 42. Calc. gas pressure, 16.729 atms. Time of setting up cell, Nov. 5, 1914. Initial pressure, 17.864 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Nov. 20, 17.082	Nov. 24, 17.259	Nov. 28, 17.180
21, 17.271	25, 17.179	30, 17.191
22, 16.960	26, 17.286	31, 17.174
23, 17.133	27, 18.368	(11 days)

Mean osmot. pressure, 17.2802 atms.

Mean ratio of osmotic to gas pressure, 1.032.

Table XVII.

0.7 Wt. normal solution. Expt. 2 at 20°. Cell 3. Resistance, 275,000 ohms. Manometer 30. Calc. gas pressure, 16.729 atms. Time of setting up cell, March 16, 1915. Initial pressure, 16.526 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
March 1, 17.069	March 4, 17.105	March 7, 17.245
2, 17.152	5, 17.147	8, 17.137
3, 17.140	6, 17.105	(8 days)

Mean osmot. pressure, 17.1375 atms.

Corr. mean osmot. pressure, 17.2711 atms.

Mean ratio of osmotit to gas pressure, 1.032.

Table XVIII.

0.8 Wt. normal solution. Expt. 1 at 20°. Cell 5. Resistance, 183,000 ohms. Manometer 44. Calc. gas pressure, 19.119 atms. Time of setting up cell, Oct. 31, 1914. Initial pressure, 19.753 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Nov. 12, 19.833	Nov. 17, 19.836	Nov. 26, 19.836
13, 19.898	18, 19.670	27, 19.780
14, 19.811	19, 19.741	28, 19.852
15, 20.006	20, 19.790	30, 19.827
16, 19.886	25, 19.792	Dec. 1. 19.731
		(15 days)

Mean osmot. pressure, 19.819 atms.

Corr. mean osmot. pressure, 19.6948 atms.

Mean ratio of osmotic to gas pressure, 1.0301.

Table XIX.

0.8 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 122,000 ohms. Manometer 44. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 6, 1914. Initial pressure, 20.824 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Dec. 23, 19.769	Dec. 27, 19.879	Dec. 31, 19.776
24, 19.806	28, 19.883	Jan. 3, 19.915
25, 19.853	29, 19.801	4, 19.887
26, 19.723	30, 19.806	(11 days)

Mean osmot. pressure, 19.823 atms.

Mean ratio of osmotic to gas pressure, 1.036.

Table XX.

0.8 Wt. normal solution. Expt. 3 at 20°. Cell 1. Resistance, 157,000 ohms. Manometer 41. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 18, 1914. Initial pressure, 21.463 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Dec. 30, 19.777	Jan. 4, 19.758	Jan. 7, 19.759
31, 19.777	5, 19.753	8, 19.734
Jan. 3, 19.654	6, 19.521	9, 19.760
		(9 days)

Mean osmot. pressure, 19.7114 atms.

Mean ratio of osmotic to gas pressure, 1.038.

Mean ratio of Expts. 1, 2, and 3, 1.034.

Table XXI.

0.9 Wt. normal solution. Expt. 1 at 20°. Cell D_6. Resistance, 157,000 ohms. Manometer 35. Calc. gas pressure, 22.509 atms. Time of setting up cell, Dec. 15, 1914. Initial pressure, 23.612 atms. Observed osmotic pressures:

Atms.	Atms.	Atms.
Dec. 28, 22.032	Jan. 2, 22.078	Jan. 5, 22.095
29, 22.014	3, 22.078	6, 22.146
30, 22.017	4, 22.091	7, 22.130
		(10 days).

Mean osmot. pressure, 22.0804. atms.

Mean ratio of osmotic to gas pressure, 1.0265.

Table XXII.

0.9 Wt. normal solution. Expt. 2 at 20°. Cell J_6. Resistance, 157,000 ohms. Manometer 37. Calc. gas pressure, 22. 509 atms. Time of setting up cell, Dec. 21, 1914. Initial pressure, 23.058 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Dec. 29, 21.907	Jan. 4, 21.894	Jan. 7, 21.951
30, 21.840	5, 21.891	8, 21.883
31, 21.849	6, 21.840	9, 21.879
		(9 days)

Mean osmot. pressure 21.8815 atms.

Corr. mean osmot. pressure, 22.029 atms.

Mean ratio of osmotic to gas pressure, 1.0242.

Mean ratio of Expts. 1 and 2, 1.0253.

Table XXIII.

1.0 Wt. normal solution. Expt. 1 at 20°. Cell 3. Resistance, 366,000 ohms. Manometer 37. Calc. gas pressure, 23.899 atms. Time of setting up cell, Oct. 24, 1914. Initial pressure, 23.226 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Nov. 28, 24.368	Dec. 2, 24.259	Dec. 7, 24.428
30, 24.390	3, 24.286	8, 24.346
Dec. 1, 24.285	4, 24.393	10, 24.373
	5, 24.324	(10 days).

Mean osmot. pressure, 24.3442 atms.

Corr. mean osmot. pressure, 24.4886 atms.

Mean ratio of osmotic to gas pressure, 1.0246.

Table XXIV.

1.0 Wt. normal solution. Expt. 2 at 20°. Cell 3. Resistance, 220,000 ohms. Manometer 32. Calc. gas pressure, 23.899 atms. Time of setting up cell, Dec. 15, 1914. Initial pressure, 25.698 atms. Observed osmot. pressures:

Atms.	Atms.	Atms.
Jan. 13, 24.375	Jan. 18, 24.450	Jan. 21, 24.512
15, 24.646	19, 24.530	22, 24.489
16, 24.375	20, 24.381	23, 24.510
		(10 days).

Mean osmot. pressure, 24.4699 atms.

Corr. mean osmot. pressure, 24.612 atms.

Mean ratio of osmotic to gas pressure, 1.030.

Mean ratio of Expts. 1 and 2, 1.0273.

Tables I to XXIV give a somewhat detailed account of each experiment. It should be pointed out that the theoretical gas pressures given in these tables are calculated by means of the equation PV = KT in which V is the colume of the solvent in the pure condition at 4 degrees Centigrade. It should be noted, also, that the value 0.00367 t has been employed in all calculations of pressure; hence in so far as this coefficient is incorrect for nitrogen gas at the higher pressures, a correction is still to be applied to the osmotic pressures recorded in the tables. Furthermore, the concentration of a few of the solutions was found to be slightly changed when the cells were taken down, and in such cases the ratios were corrected for the resulting dilution or concentration.

The mean ratio by concentrations of all 24 determinations is tabulated below, and compared with the corresponding value for 30° - 50° as recorded by Dr. Holland and Mr. Musselman:

	0.1 N	0.2 N	0.3 N	0.4 N	0.5 N
10°	1.034				
20°	1.035	1.030	1.028	1.014	1.0246
30°- 50°	1.000	1.001	1.001	.999	1.006

	0.6 N	0.7 N	0.8 N	0.9 N	1.0 N
20°	1.031	1.032	1.034	1.0253	1.0273
30°- 50°	1.000	1.006	.999	1.000	1.000

Conclusions.

The osmotic pressure of all concentrations of glucose solutions from 0.1 to 1.0 weight normal at 20°, and the 0.1 weight normal so-

lution at 10°, has been shown to differ in a marked manner from the values that have been obtained from 30° to 50°. At the latter temperatures all concentrations obey the equation of Van't Hoff PV = KT, using the weight normal system; that is, the ratios are unity throughout, whereas all of the ratios at 20° and 10°, for the one solution studied, are above unity. These ratios, moreover, do not show a regular increase with increase in concentration, as do cane sugar solutions at the same temperatures.

If hydration be the cause for the excess of osmotic over gas pressure, it is, at 20°, independent of the concentration. Furthermore, the same excess of gas above osmotic pressure is found at 20° as at 10°, indicating that, if hydration be the cause of the excess pressure, this hydration is the same at 20° as at 10°. As is shown in the above table, the excess pressure disappears between 20° and 30°, which suggests that between these temperatures the "hydration" of glucose in aqueous solutions disappears.

Biography.

Walter H. Coolidge was born December 13, 1890, at Cincinnati, Ohio. His early education was obtained in the public schools of that place, graduating in the spring of 1908. In the fall of that same year he entered Kenyon College, Gambier, Ohio, and graduated in 1912, receiving the degree of Bachelor of Philosophy. In 1912 he entered the graduate department of Johns Hopkins University, majoring in Chemistry with Physical Chemical and Geology as his first and second subordinate subjects respectively. He was assistant in Chemistry at Kenyon College during the academic years 1909 - '12.